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ALTERATION OF ACTIVE SUBSTANCE CONTENT IN "HEXACHLORAN DUST" PESTICIDE FORMULATION AT EXPOSURE TO ELECTRON BEAM

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Abstract

The most popular methods of organochlorinated pesticides (OCP) destruction, which are based on thermal dechlorination, are not ecologically safe. The other process – radiation-chemical degradation – has got some advantages. It does not involve high temperatures and expensive reagents. In this study, the effective OCP degradation was observed under irradiation of residuals of the active substance of 'Hexachloran dust' pesticide formulation, intended for utilization. Parameters for the preparation powder (dry form) exposure to electron beam are discussed. It is shown that at the exposure to electron beam at dose of 100 kGy, the degradation degree of hexachlorocyclohexane (HCH) isomers in a composition of active substance achieves 56.2–66.3%.

Keywords: organochlorinated pesticide; irradiation; electron beam; radiation stability; dose and dose rate of radiation; pesticide formulation; hexachlorocyclohexane; radiation degradation

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For more than a decade, researches have been continuing to identify the most effective ways to eliminate the organochlorinated pesticides (OCP) itemized in the list of persistent organic pollutants (POPs) prohibited for production and use [1]. Nevertheless, a making decision on the methods for their utilization is kept being a challenge for many countries and stakeholders. Issues and procedures of management for this type of waste are usually considered at the legislative level. For example, the Brazilian federal law establishes a responsibility for the removal of pesticides for those industries that are directly or indirectly related to the toxicants. This law obliges the producers

carrying out researches to advance new technologies for the recovery and utilization of material containing OCP [2]. The Russian national program for the POPs (including OCP) disposal provides for a development of effective and ecologically safe technologies for their destruction [3]. An incineration is considered as the most technologically advanced and effective way to destroy organochlorine hydrocarbons. There are special requirements to exclude the possibility of an OCP transforming into more toxic substances (like dioxins, for example): short stay in the reaction zone; high temperatures; providing of turbulence and high oxygen consumption [4]. Similar requirements are applied at a utilization of polychlorinated biphenyls (PCBs). This way of the pesticides and PCBs destruction during their high-temperature combustion is admitted based on the long industrial experience of different countries [5]. However, this method is quite energy-intensive. This makes a complete utilization of all nowadays existing persistent organochlorine hydrocarbons impossible through their combustion. Thus, the development and introduction of another techniques is necessary [4].

Recently, attention has been attracted to an application of non-traditional destructive techniques (such as mechanochemistry, plasma chemistry, various types of radiation exposure, etc.) for treatment and recycling of natural gas, gas condensates, oil and oil products. From the scientific point of view, these techniques deal with the dynamics of molecular reactions and energy redistribution processes which aimed at an alteration of the of hydrocarbon feedstock's fundamental properties without using catalytic methods and refining the products of primary oil refining [6]. These new techniques for hazardous substances destruction are now considered as an alternative to the incineration because of the environmental issues. There are examples of patents and licenses for the application of ionizing radiation at technical radiation facilities to destroy organic substances [7-8]. One of the common issues discussed at national and international scientific meetings is the development of technologies utilizing energy of electronic and other types of radiation [9-10]. For example, specific projects are proposed to neutralize soils by destroying toxic pollutants with electron irradiation [9]. Studies are underway about the pesticides utilization too. Thus, C.L. Duarte et al. investigated the irradiation conditions for the pesticide residues degradation in the processing of packaging material [2, 11-13]. Both gamma and electron radiation applications were considered. They showed that the complete removal of active substance (chlorpyrifos) of the pesticide formulation from packaging material was achieved by irradiation at dose of 25 kGy with triple washing-out of the preparation with water [2]. In another work it was found [11] that the electron beam can be applied for the destruction of various pesticides. The authors also demonstrated that at an absorbed

dose of 50 kGy (with gamma and electron irradiation) approximately equal amounts of pesticides were degraded (slightly more than 60%) [12]. The presence of water activated the chlorpyrifos degradation process under electron irradiation, i.e. in this case the pesticide degradation after irradiation at a dose of 20 kGy increased by 20-30% [13].

Mainly, in the above mentioned works, technical substances that do not belong to highly hazardous pesticides were exposed to irradiation [14]. An objective of this study is to consider an alteration under radiation exposure in the active substance – hexachlorocyclohexane (HCH) – as the component of the 'Hexachlorane dust' pesticide formulation, which is included in the POPs list. Findings from studying the HCH radiation stability at gamma-irradiation are presented in [15-17]. In this work, the radiation-chemical stability of the active substance under radiation exposure to electron beam is studied for the composition of a pesticide formulation in dry form.

1. Materials and methods

The 'Hexachloran dust' pesticide formulation, intended for utilization, was substituted for radiation exposure. Detailed information on this pesticide formulation is given in the previously published studies that were carried out with gamma-radiation [15-17].

Electronic irradiation was carried out in doses of 10, 44, 100, 120, 150 and 200 kGy given by the radiation-technological unit (RTU) with an UELR-10-10-40 accelerator. The samples of the pesticide formulation were irradiated in various forms: a water-alkaline suspension of dust, a dry powder of preparation and a dry powder of lindane. At each radiation dose, several samples (3-7) were irradiated; each sample was arranged as a container (test-tube or weighing bottle) with pesticide formulation in a given form. The test-tubes are made of glass, in the form of a cylinder of 17 cm in length and 1.5 cm in diameter (with a stopper), intended for chemical, biological and microbiological laboratory procedures. Large (weight 28 g, label 30x40) and small (weight 8.15 g, label 20x30) glass weighing bottles were used. Here, the findings are presented from irradiation of the 'Hexachloran dust' dry powder in large weighing bottles.

Before the preparation irradiation, a dose ratio in the containers and the reference point was determined. For this purpose, an empty test tube or weighing bottle containing a detector was exposed, and also a detector was placed in the reference point. The reference point was located on the outer lateral surface of the box facing the electronic beam. For dose measurements, SO AD(F)R 5/50 detectors were used. This

kind of detectors is admitted as a state standard for the measurement of absorbed dose of photon and electron radiation in water in the range of 5–50 kGy. The RTU installation was applied in the following regime: the energy of beam electrons of 10 MeV; the average beam current of 790 μA; the conveyor speed of 1.045 m/min (1.1 relative units). The data on dose measurements are shown in Table 1.

Table 1: Detector-recorded dose at the reference and experimental points in preliminary measurements (empty containers).

Location of detector	Dose, kGy (P = 0.95)
Reference point	17.9 ± 1.6
Inside a weighing bottle (small)	18.8 ± 1.8
Inside a weighing bottle (large)	19.2 ± 1.6
Inside a test-tube	19.1 ± 1.8

Irradiation was delivered via multiple transmission of a transport container (box) with samples, placed on the conveyor belt, through the electron-beam; at this, the necessary dose value was supplemented step-by-step. As soon as the required dose was reached in a certain cycle by a set of samples, this set was removed from the transport container. A total of 13 cycles were done. In the first cycle, a dose of 10 kGy was planned to deliver and a dose of 16 kGy in each subsequent cycle. Based on the RTU technical characteristics, the irradiation with the electron beam energy of 10 MeV was carried out under following operating conditions of the accelerator:

- to give a dose of 10 kGy in the first cycle: the average beam current of 755 μA; the conveyor speed of 1.9 m/min (2.0 relative units);
- to give a dose of 16 kGy in each subsequent cycle: the average beam current of 790 μA; the conveyor speed of 1.24 m/min (1.307 relative units).

During irradiation process, dose measurements were carried out. One or two detector were placed in the reference point and then removed (and replaced with another) together with sets of samples when the required dose was obtained to determine the total dose absorbed by the irradiated samples. In total, 10 detectors were used. For several samples, an additional irradiation required to obtain the planned dose levels; this was also accompanied with the dose measurements by the detectors (SO AD(F)R 1/10 detectors were used for doses less than 10 kGy, and SO AD(F)R 5/50 detectors for dose more than 10 kGy). The data on dose measurements at the samples irradiation with electron beam are presented in Table 2.

Table 2: Absorbed radiation dose at the 'Hexachloran dust' samples irradiation on the RTU.

Set number	Dose intended, kGy		Total dose delivered, kGy	
	Reference point	Samples	Reference point	Samples (coefficient 1.06)
1	9.43	10	9.3 ± 0.8	9.9 ± 1.3
2	41.51	44	41.3 ± 2.1	43.8 ± 5.1
3	94.34	100	94.1 ± 4.1	99.7±11.2
4	113.21	120	114.0 ± 4.7	120.8 ± 13.5
5	141.51	150	143.0 ± 4.6	151.6 ± 16.4
6	188.68	200	190.3 ± 5.6	201.7 ± 21.7
Note: Result and uncertainty of the measurements with a coverage factor of 2 at P = 0.95 [18].				

The initial and irradiated samples of the 'Hexachloran dust' pesticide formulation were analyzed for the content of three stereoisomers of the active substance – α-, β-, γ-HCH. The active substance was extracted with hexane. Methods of sample preparation for irradiation are presented earlier [15-17]. The experiment on sample irradiation and subsequent sample preparation for chemical analysis was carried out in triplicate. Samples analysis was carried out on GC Crystal-5000.1 chromatographic installation (Russia) in the column temperature programming mode. Statistical processing of data was done with MS Excel 2016 and Origin 2015.

2. Results

According to the chromatographic analysis data on the concentrations of each component of the active substance of the preparation, determined in the samples before and after irradiation, the decomposition degree (P, %) was calculated. This indicator was used earlier when studying the stability of the same components at gamma irradiation [12-14]. P does not depend on the initial concentration of the substance. It can be used both to compare the radiation stability of different HCH isomers under the influence of the same type of radiation, and to compare the data on irradiation with gamma quanta and accelerated electrons. The obtained results from electron irradiation are presented in Tables 3-4.

Table 3: Concentrations of HCH isomers in the 'Hexachlorane dust' preparation before and after electron irradiation.

Active substance	⟨C⟩ ± ΔC*, %			
	before irradiation	D = 10 kGy	D = 100 kGy	D = 200 kGy
α-ГХЦГ	9.28	5.17	3.37	3.27
β-ГХЦГ	2.58	1.30	1.13	0.73
γ-ГХЦГ	1.84	1.07	0.62	0.58
Σ ГХЦГ	13.70	7.54	5.12	4.58
* The measurement error was 15-30 %.				

Table 4: Degradation degree of HCH isomers in the 'Hexachlorane dust' preparation before and after electron irradiation.

Active substance	⟨P⟩ ± ΔP, %		
	D = 10 kGy	D = 100 kGy	D = 200 kGy
α-ГХЦГ	44.29	63.69	64.76
β-ГХЦГ	49.61	56.20	71.71
γ-ГХЦГ	41.85	66.30	68.48
Σ ГХЦГ	44.96	62.63	66.57

3. Discussion

Data on the initial concentrations of the HCH isomers may indicate a significant degradation of pesticide formulation (Table 3). As it was mentioned, the 'Hexachlorane dust' preparation is a kind of waste which storage time is uncertain. Significantly higher concentrations of the stable α-HCH component compared to the less stable γ-HCH indicate that the preparation was long kept unclosed, which resulted in the disproportion of isomers content compared to their concentrations in the commercial pesticide formulation. The HCH isomers' concentrations decreased in the process of electron irradiation with increasing of absorbed dose (Table 3).

According to the P values given in Table 4, all HCH isomers are capable of degradation at radiation exposure. Their degradation degree is similar for the given absorbed dose level. This may indicate the presence of a unified mechanism of radiation effect, where the spatial structure of an isomer molecule does not affect an activity of radiochemical transformations. An alteration in the P value with increasing absorbed dose from 10 to 100 kGy amounts to 20-30% on average. It is interesting that the radiation

degradation α- and γ-HCH is slowing down when doses enhance 100 kGy (for β-HCH, additional studies are planned). These data are consistent with the dose dependency obtained in other works [12-13] for pesticides. It was found that maximum degradation of chlorpyrifos pesticide of P=80% could be achieved at 20 kGy, and further with an increasing dose of up to 100 kGy, the P value remains practically unchanged and keeps within 85-90%.

From data in Table 4 as well as findings of other studies [15-17], it follows that, in comparison with gamma quanta, the electron beam irradiation leads to a greater degree of HCH molecules destruction. Thus, at gamma-radiation exposure at doses of 10 and 44 kGy (dose rate 0.51 Gy/s) the P values for all HCH isomers were within the measurement uncertainty range [15], and the degradation degree which did not exceed 7.2%, was determined with good confidence only for γ-HCH at a dose of 117 kGy (dose rate of 0.28 Gy/s) [17]. A slight decline in the concentration (according to calculations for P less than 10%) of PCB isomers was also shown at gamma irradiation of transformer oil ('Sovol 10' trade mark) at a dose of 250 kGy [19].

At the same time, it was found [12] that in the presence of water at an absorbed dose of 50 kGy, approximately the same amount of pesticides (slightly more than 60%) was destructed both by gamma rays and by using an electron beam accelerator. In our studies at gamma irradiation conditions [17], the degradation degree of γ-HCH in aqueous-alkaline suspension of 'Hexachlorane dust' was shown to be four times higher than for dry dust. It is interesting to follow this effect at the accelerated electron irradiation.

4. Conclusions

The studies implemented show an effectiveness of an application of electronic beam for the destruction of the HCH in the composition of the active substance of the dry pesticide preparation "hexachlorane dust" (up to 60-70% of the decomposition at the absorbed dose of 200 kGy). The comparison of the obtained data with the literature (similar in type of radiation), as well as the results of HCH gamma irradiation indicate that the degree of electronic decomposition of the pesticide can be increased by changing the aggregate state of the sample without increasing the dose of radiation exposure.

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